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by

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Abstract

The development of laboratory instrumentation systems for investigating the gas-phase thermal decomposition behavior of organic materials has evolved over the past ten years. In these systems, high-temperature tubular reactors are used for the controlled thermal exposure of different gas-phase substances. Gas chromatography has been the major analytical technique for determining the extent of thermal decomposition and the formation of various products of incomplete combustion. The evolutionary development of laboratory instrumentation covering seven thermal systems is summarized. Examples are presented of the application of laboratory studies to the controlled high-temperature incineration of industrial organic wastes.

Introduction

Modern industrial society is faced with the task of recycling, detoxifying, or appropriately disposing of vast quantities of industrial organic waste. Controlled high-temperature incineration is considered one of the most promising methods for permanent disposal. Before large-scale industrial waste incineration can be fully implemented, it is necessary to have a more definitive understanding of incineration processes and the thermal destruction behavior of organic substances. Thermal decomposition studies are being conducted on laboratory-scale, pilot-scale, and large-scale incineration units.

There are numerous variables associated with the thermal destruction of organic substances. Therefore, the incineration of a complex multiphase organic mixture is extremely complicated. Fortunately, meaningful studies of the gas-phase thermal decomposition behavior of pure organic substances and complex mixtures can be conducted in the laboratory with specially designed thermal instrumentation systems. By their nature, laboratory-scale experiments can provide precise control over many important variables, and as only very small quantities of sample are needed, these tests can be conducted safely.

In the following, the development of seven laboratory-scale thermal instrumentation systems is summarized. Also, the need for these laboratory assemblies is discussed along with the events leading to their development. Each thermal system is briefly described using a block diagram format, and

for each, an application is presented whereby it was used for obtaining gas-phase thermal decomposition data.

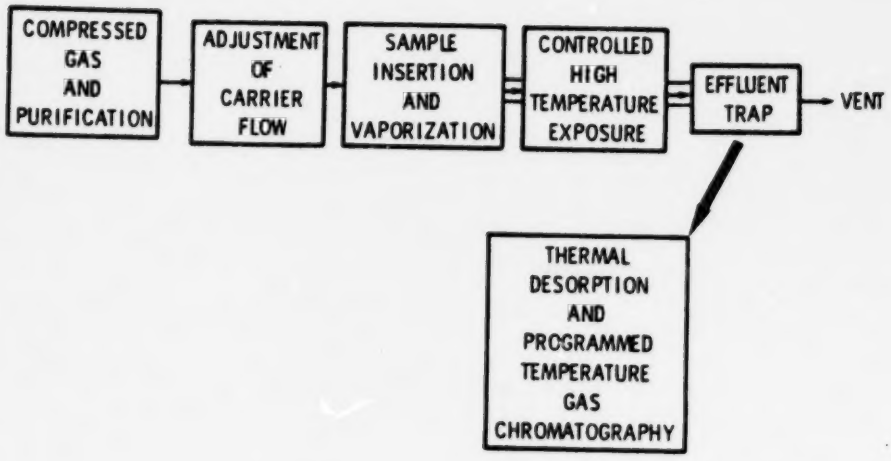
Descriptions of the Various Laboratory-Scale Thermal Instrumentation Systems

In 1974, a discontinuous thermal system (DTS) was developed at the University of Dayton for studying the thermal decomposition behavior of chlorinated pesticides. The DTS was developed under the sponsorship of a US-EPA grant[1], and was used extensively for studying the thermal decomposition behaviors of DDT, Kepone, Mirex, and other chlorinated pesticides. A block diagram of the DTS is shown in Figure 1a. This discontinuous assembly was designed primarily for testing low volatility materials, such as pesticides and other high-molecular-weight chlorinated hydrocarbons.

After the sample has been admitted to the DTS and gradually vaporized, it is subjected to a controlled-thermal exposure by passing the gaseous material through a narrow-bore quartz tubular thermal reactor. The unreacted parent compounds and the products of incomplete combustion (PICs) are then trapped within an in-line filter. This collection trap is then detached from the thermal reactor portion of the system and inserted into a modified programmed-temperature gas chromatograph where, after thermal desorption, the contents of the collection trap are subjected to gas chromatographic analysis.

Figure 1b shows some interesting data obtained using the DTS. This figure represents the thermal decomposition profile

(a)



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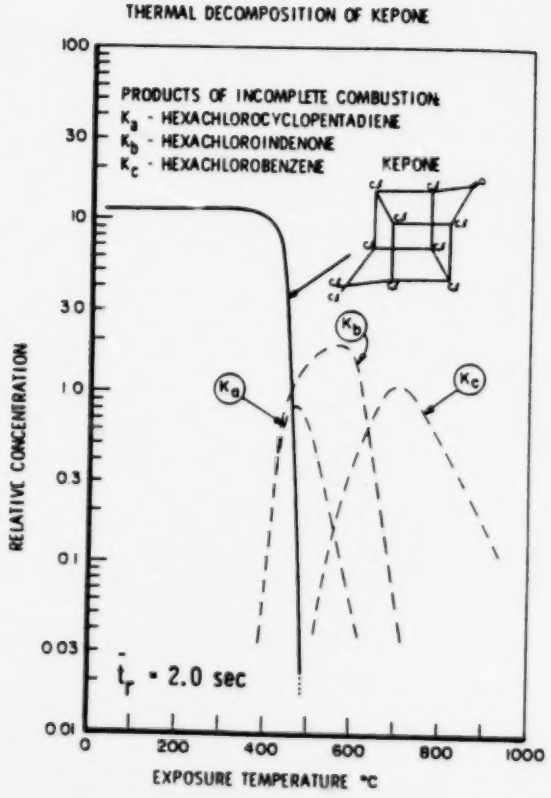
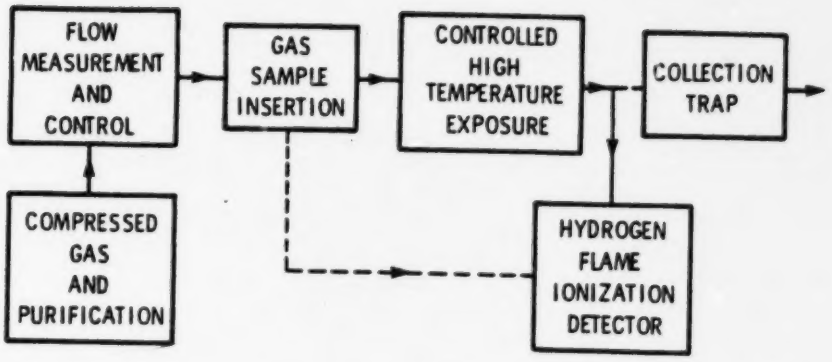


Figure 1. Discontinuous thermal system (DTS) and Kepone® thermal decomposition data.

for the pesticide Kepone, a compound reported to be carcinogenic in animals. It is apparent from this figure that practically all of the Kepone has been thermally decomposed prior to reaching an exposure temperature of 932°F (500°C). However, notice the K_a, K_b, and K_c profiles which correspond to other toxic chlorinated compounds. These are stable PICs that were formed during the thermal decomposition of Kepone. This information illustrates an important point. It can be concluded from these data, that beyond the thermal decomposition of the parent substance, one must also consider the thermal stability and toxicity of the stable products of incomplete combustion that can be formed during high-temperature reactions[2].

In the middle 1970's a system developed at the Union Carbide Corporation was used to subject numerous gaseous samples to controlled high-temperature exposures[3,4]. Figure 2a is a block diagram of this system, referred to here as the Union Carbide System (UCS). The UCS also uses a narrow-bore quartz tubular reactor maintained in a precisely controlled high-temperature furnace where the assembly has been employed primarily for oxidation studies, as in most cases the flowing atmosphere has been air. The UCS uses an in-line hydrogen flame ionization detector for continual monitoring of effluent organics. It also has features for collecting exhaust samples and subjecting the collected products to subsequent instrumental chemical analyses.

(a)



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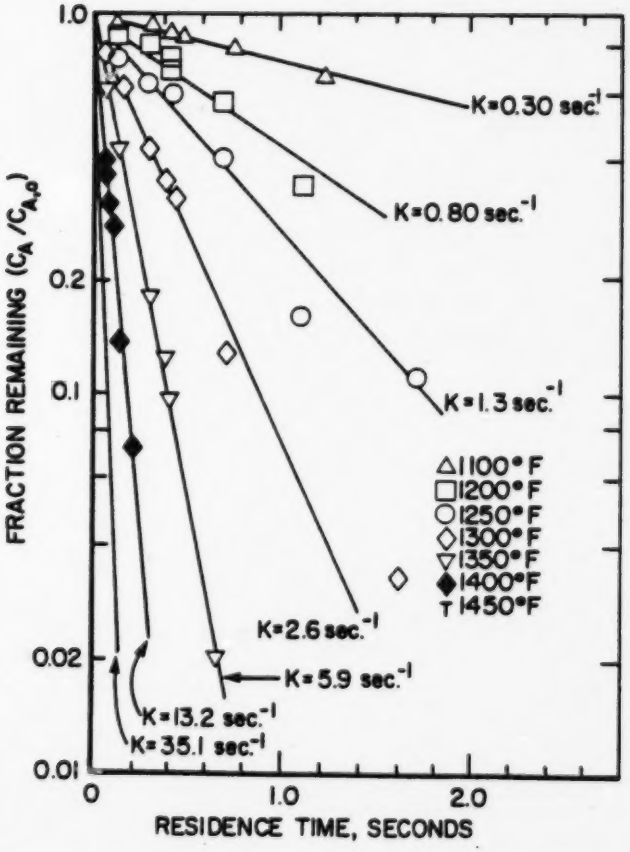


Figure 2. Union Carbide's system (UCS) and vinyl chloride thermal decomposition data.

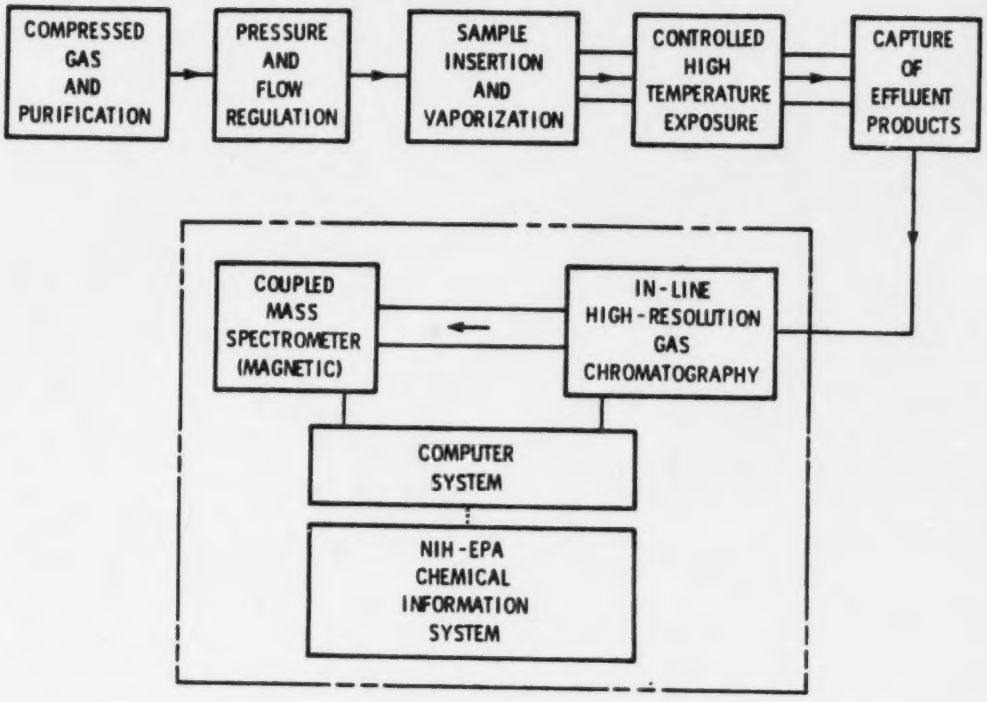
An example of data obtained with the UCS is shown in Figure 2b. These thermal decomposition profiles correspond to the destruction behavior of vinyl chloride. This particular graph shows that the extent of thermal decomposition of vinyl chloride is a well-ordered function of the gas-phase residence time. The researchers at Union Carbide have also used this instrumentation system for studying the gas-phase kinetics of numerous volatile organic substances[5].

The previously described Kepone data showed the importance of detecting, identifying, and quantitating PICs. Consequently, a sophisticated thermal decomposition analytical system (TDAS) was designed and developed in the latter 1970's at the University of Dayton to fulfill this need[6].

Figure 3a is a block diagram of the TDAS, showing that it is a closed continuous system which employs an in-line gas chromatograph-mass spectrometer for separation, quantification, and identification of the various substances that have passed through the thermal reactor. The TDAS requires only a very small amount of sample (micrograms or less) for conducting thermal decomposition studies. Figure 3b is a tabulation obtained from TDAS studies showing some of the major PICs that have been formed from various parent substances. It is interesting to note that many of these PICs are highly toxic compounds.

Another thermal instrumentation system which can accommodate larger quantities of sample is shown in Figure 4a.

(a)

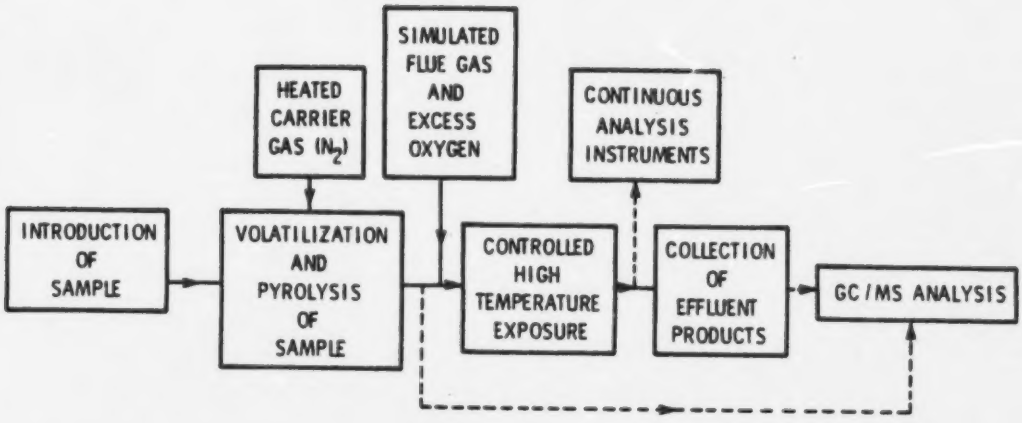


(b)

PARENT SUBSTANCE	MAJOR PICs
KEPONE	HEXACHLOROBENZENE HEXACHLOROCYCLOPENTADIENE HEXACHLOROINDENONE
MIREX	HEXACHLOROBENZENE
DDT	DDE
PENTACHLORONITROBENZENE	HEXACHLOROBENZENE
PCBs	CHLORINATED BENZENES CHLORINATED FURANS BIPHENYL OTHER PCBs
HEXACHLOROCYCLOPENTADIENE	HEXACHLOROBENZENE
CHLOROFORM	TETRACHLOROETHYLENE PENTACHLOROETHANE

Figure 3. Thermal decomposition analytical system (TDAS) and summary of observed products of incomplete combustion.

(a)



(b)

EXPOSURE TEMPERATURE (°C)	MEAN RESIDENCE TIME (sec)	HCCPD INPUT RATE (g/min)	DESTRUCTION EFFICIENCY (%)
400	0.33	3.0×10^{-3}	0
600	0.30	2.9×10^{-3}	90.
800	0.36	2.8×10^{-3}	99.992
1000	0.32	3.0×10^{-3}	99.993
1200	0.30	3.0×10^{-3}	99.997

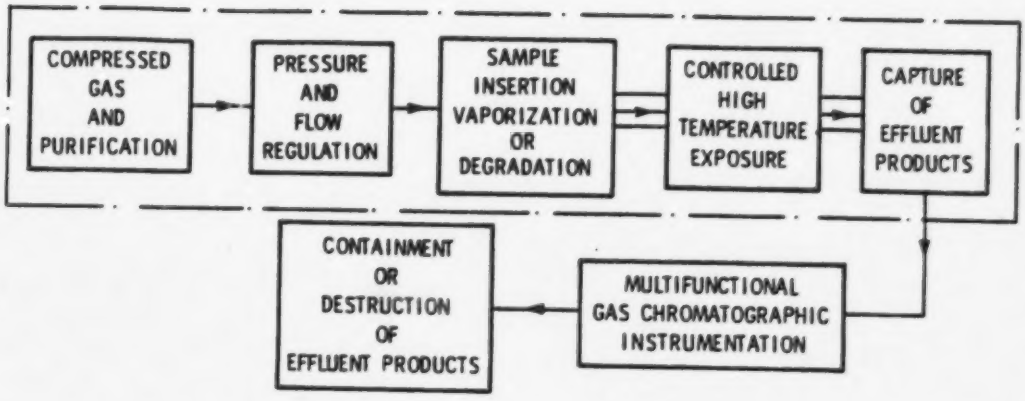
Figure 4. Midwest Research Institute's system (MRIS) and hexachlorocyclopentadiene thermal decomposition data.

This block diagram depicts the Midwest Research Institute's laboratory-scale hazardous waste incineration system (MRIS), which was designed primarily for subjecting samples to thermal decomposition studies prior to trial incineration burns. The MRIS can be operated in a batch-fed mode or it can be used in a continuous liquid injection mode. It can also accommodate gram-size quantities of nearly any form of waste, including liquids, solids, slurries, sludges, etc.

Figure 4b is a tabulation of results obtained from a series of tests where a hexachlorocyclopentadiene/cyclohexane solution was subjected to a series of high-temperature oxidative exposures. Although hexachlorocyclopentadiene was efficiently destroyed at the higher exposure temperatures, numerous PICs were observed throughout this series of tests.

Most of the thermal instrumentation systems presented thus far require considerable time for a single laboratory determination. With these systems, it is not uncommon for each test to require up to two hours for completion of all of the activities associated with a single experiment. To obtain thermal decomposition data more rapidly, and simultaneously to enhance the detection capability for trace levels of PICs, a thermal decomposition unit-gas chromatographic system (TDU-GC) was developed at the University of Dayton[7]. As shown in Figure 5a, the TDU-GC uses the same design of thermal decomposition unit that was incorporated into the TDAS already discussed. However, the TDU-GC employs a

(a)


COMPRESSED GAS AND PURIFICATION
PRESSURE AND FLOW REGULATION
SAMPLE INSERTION VAPORIZATION OR DEGRADATION
CONTROLLED HIGH TEMPERATURE EXPOSURE
CAPTURE OF EFFLUENT PRODUCTS
MULTIFUNCTIONAL GAS CHROMATOGRAPHIC INSTRUMENTATION
CONTAINMENT OR DESTRUCTION OF EFFLUENT PRODUCTS

(b)

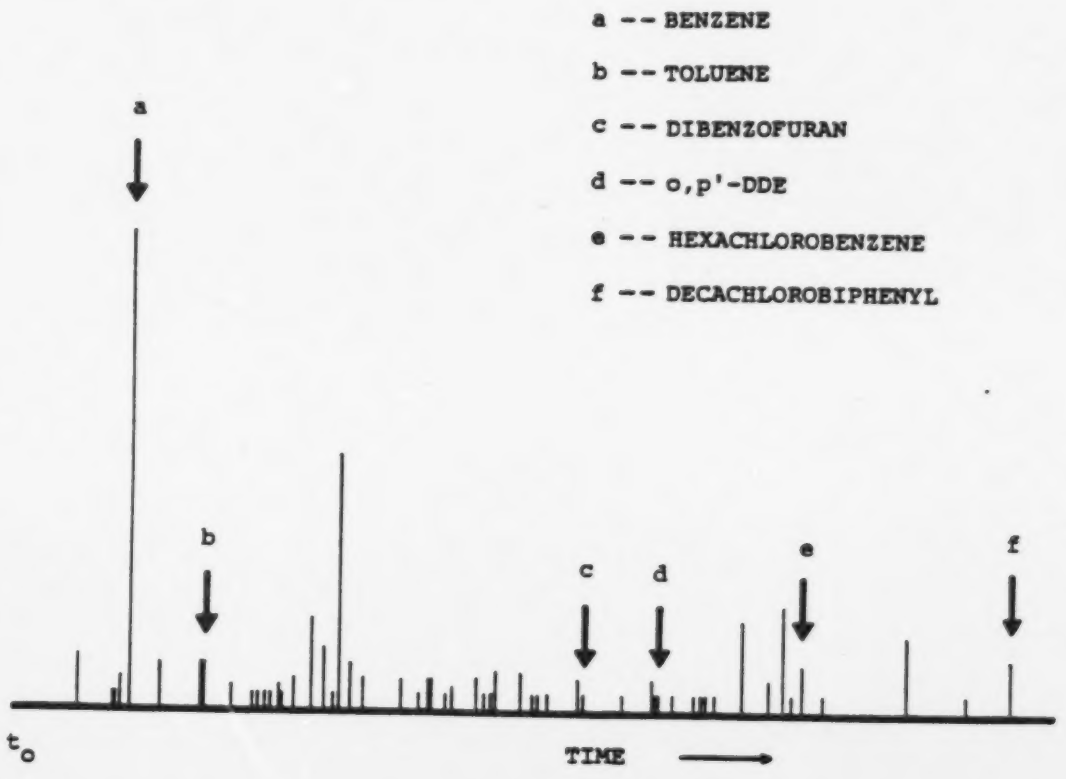


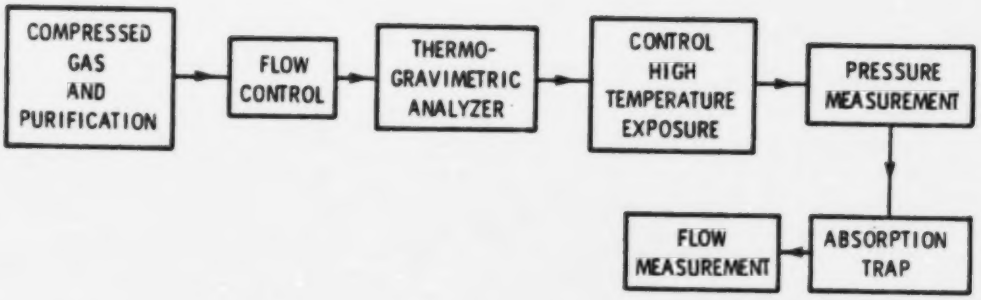
Figure 5. Thermal decomposition unit-gas chromatographic system (TDU-GC) and observed stable thermal reaction products.

multifunctional gas chromatograph for analysis of the effluent products. Although the TDU-GC does not have the chemical compound identification power of the TDAS (with its mass spectrometer) it is capable of obtaining thermal decomposition data in less than one hour per experiment. It can also handle extremely complex organic mixtures and it readily detects thermally stable PICs that survive the various high-temperature exposures.

Figure 5b is a skeletal chromatogram which indicates some of the stable PICs that resulted from subjecting an extremely complex industrial organic waste mixture to a 1,274°F (690°C) exposure while in flowing air[8]. In the opinion of many, it is these stable PICs which would most seriously challenge a high-temperature incineration system.

The thermal data generation system (TDGS) depicted in Figure 6a was developed at the Wastewater Technology Centre of Canada's Environmental Protection Service and employs a narrow-bore quartz tubular thermal reactor[9,10]. However, the TDGS uses a thermogravimetric analyzer for admitting the sample to the reactor and thereby provides a readily adjustable method for controlling the mass throughput of sample. The TDGS was originally designed for thermally testing very complex multi-phase samples such as wood waste products, pesticide wastes, sludges, etc. Figure 6b shows some TDGS data which resulted from thermal decomposition studies of pentachlorophenol and pentachlorophenol treated wood wastes. Pentachlorophenol is an agent that has been used extensively in the preservation

(a)



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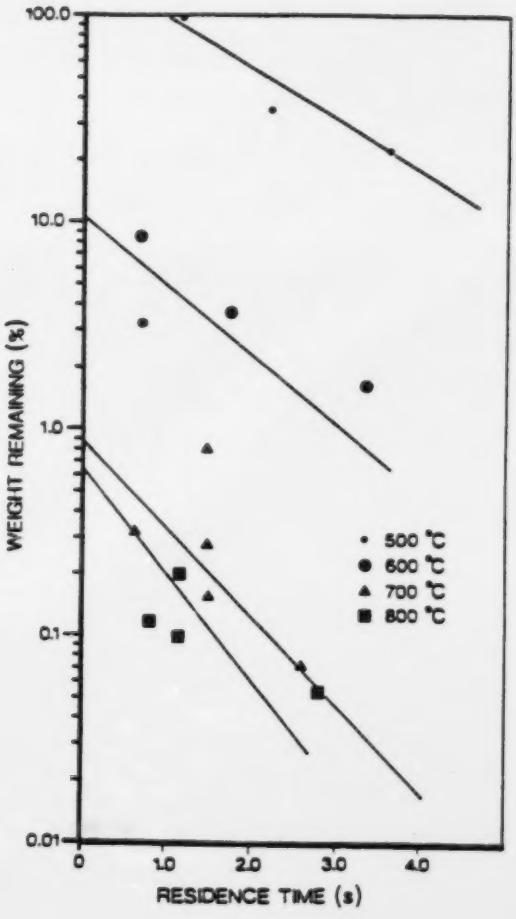


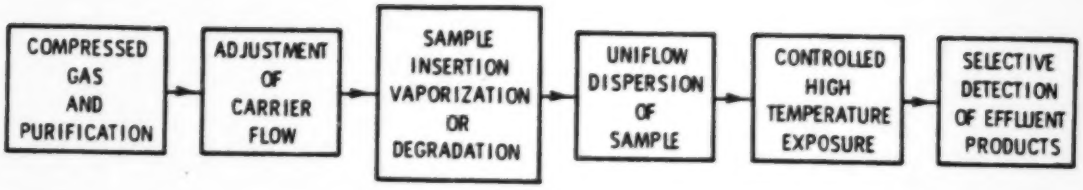
Figure 6. Thermal data generation system (TDGS) and pentachlorophenol thermal decomposition data.

and treatment of wood. Recent studies have indicated that pentachlorophenol may be a precursor of several highly toxic chlorinated aromatic compounds. Accordingly, considerable interest is centered around the thermal destruction of pentachlorophenol treated materials.

At a recent ASME/EPA conference on hazardous waste incineration (the Williamsburg Conference of 1981) there was considerable interest in developing procedures for ranking the incinerability of different organic substances. In view of this interest, a packaged thermal reactor system (PTRS) was developed under US-EPA sponsorship for rapidly evaluating the thermal stability of different organic substances[11]. From the diagram of the PTRS in Figure 7a, it is seen that this is a relatively simple system (no chromatographic instrumentation, etc.) capable of rapidly generating thermal decomposition data for numerous different organic substances and conducting a single experiment in less than 15 minutes.

Figure 7b shows some of the thermal decomposition data obtained with the PTRS. Thermal decomposition curves for three compounds are shown in this figure, and it is seen that nitrobenzene and aniline have lesser thermal stabilities than tetrachloroethylene. However, additional studies also showed that while tetrachloroethylene did not tend to produce significant levels of PICs, aniline and nitrobenzene produced abundant products of incomplete combustion.

(a)


COMPRESSED GAS AND PURIFICATION
ADJUSTMENT OF CARRIER FLOW
SAMPLE INSERTION VAPORIZATION OR DEGRADATION
UNIFLOW DISPERSION OF SAMPLE
CONTROLLED HIGH TEMPERATURE EXPOSURE
SELECTIVE DETECTION OF EFFLUENT PRODUCTS

(b)

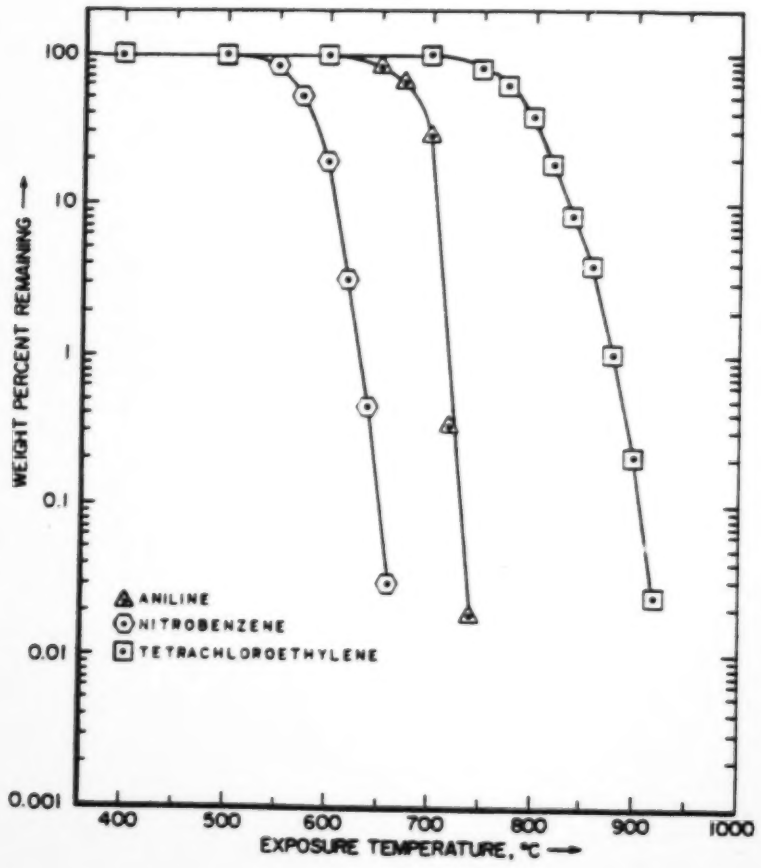


Figure 7. Packaged thermal reactor system (PTRS) and aniline, nitrobenzene, and tetrachloroethylene thermal decomposition data.

Data obtained from the seven thermal decomposition systems discussed thus far have provided valuable information on the gas-phase thermal decomposition behavior of different organic substances. Much has also been learned about the variables which affect gas-phase thermal decomposition behavior. Figure 8 lists those important gas-phase thermal decomposition variables elucidated thus far. To obtain a better understanding of these gas-phase variables, their interactions, and their effects in different scale units, e.g., laboratory-scale, pilot-scale, and full-scale, other studies are already underway. Tests using a pilot-scale rotary kiln/afterburner incinerator are being conducted at the EPA's Combustion Research Facility in Jefferson, Arkansas. Studies using a turbulent flame reactor in intermediate-scale tests are being conducted at EPA's Center Hill Laboratory in Cincinnati, Ohio.

As a result of the design activities and the sum of the experiences gained from these systems, a universal thermal instrumentation system[12] is now under development and it is referred to as a system for thermal decomposition studies (STDS). From the diagram of the STDS shown in Figure 9a, it is seen that this system uses internally interchangeable test cells for subjecting organic substances to high-temperature exposures. It also employs externally interchangeable equipment for preparative work and further special analyses of the effluent. This is a universal laboratory-scale system which can incorporate both flame and nonflame environments.

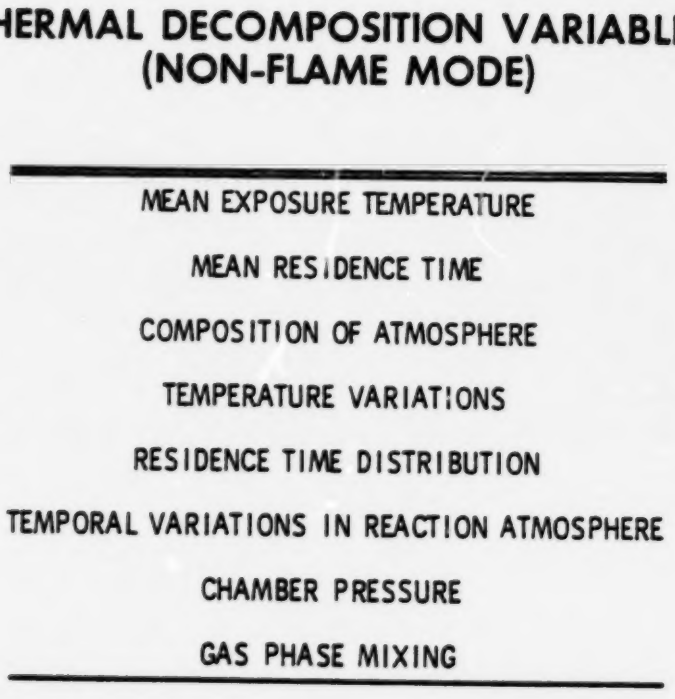
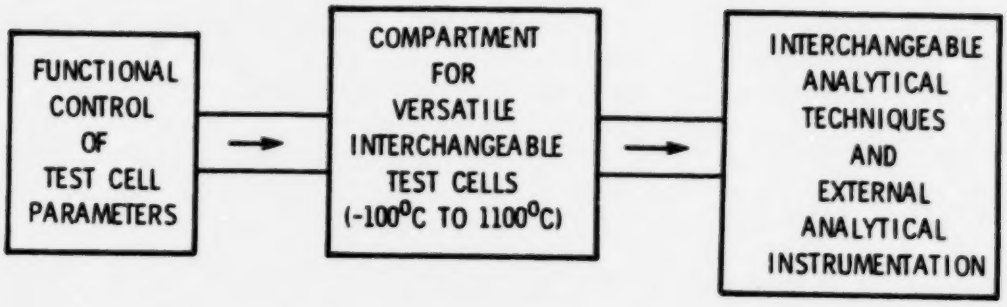


Figure 8. Important variables and parameters associated with non-flame gas-phase thermal decomposition behavior.

(a)


FUNCTIONAL CONTROL OF TEST CELL PARAMETERS
COMPARTMENT FOR VERSATILE INTERCHANGEABLE TEST CELLS (-100°C TO 1100°C)
INTERCHANGEABLE ANALYTICAL TECHNIQUES AND EXTERNAL ANALYTICAL INSTRUMENTATION

(b)

INTERCHANGEABLE TEST CELLS DESIGNED FOR:

- THERMAL DECOMPOSITION EXPERIMENTS
- HIGH-TEMPERATURE PHYSICAL SIMULATIONS

Figure 9. Functional description of system for thermal decomposition studies (STDS).

The key feature of the STDS is the interchangeable test cell concept which permits tremendous versatility in conducting laboratory-scale studies (see Figure 9b). The STDS is designed to determine the thermal decomposition behavior of pure substances and complex industrial organic mixtures. It is also capable of identifying and ranking the variables which affect the gas-phase thermal decomposition of organic substances.

In summary, laboratory-scale thermal instrumentation systems have been found to be of value with respect to studying the gas-phase thermal decomposition behavior of organic substances. Laboratory systems are especially suited for:

(1) determining the thermal destruction properties of parent organic substances,

(2) the detection of stable products of incomplete combustion,

(3) identifying and evaluating important variables or operational parameters which effect the high-temperature decomposition process, and

(4) providing guidance information for subsequent pilot-scale or eventual full-scale incinerations of industrial organic wastes.

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Credits

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